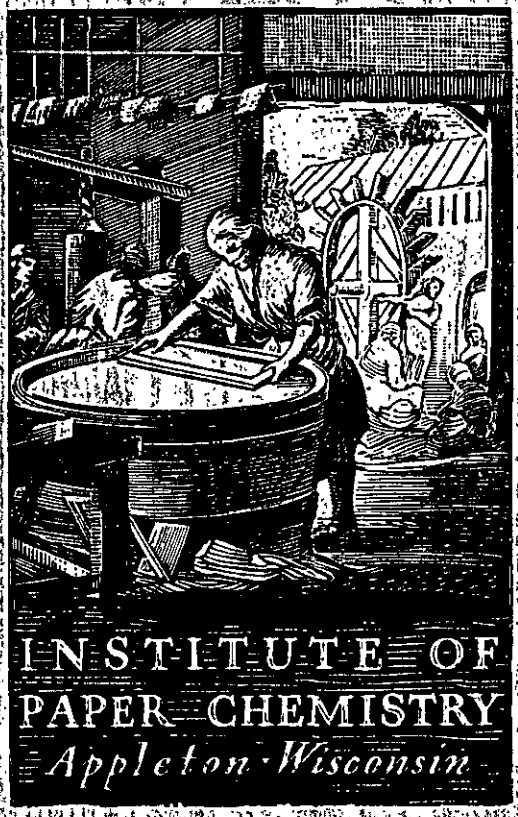

CONFIDENTIAL

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS: CHEMICAL RECOVERY

Project 2500

Report Twenty-One

A Progress Report

to

THE GRANTORS

July 6, 1973

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

On the basis of the work which has been completed, it can be concluded that workable chemical recovery systems for the holopulping process will be available when required. No new technical breakthroughs are required. There appear to be no technical roadblocks to successful chemical recovery.

Two recovery concepts are available, depending on the proportions of sodium and chlorine in the spent liquor. When a large amount of chlorine is present, the recovery process will consist of: evaporation to about 40% solids, fluidized bed incineration to produce NaCl (possibly requiring the scrubbing of HCl from the flue gas), electrolysis of NaCl to form Cl_2, H_2, and NaOH, burning H_2 and Cl_2 to form HCl, and ClO_2 production by the HCl process. When sodium is the dominant chemical, the recovery process will consist of: evaporation to 60-65% solids, combustion in a soda-type recovery furnace, causticizing the resulting Na_2CO_3-NaCl mixture, evaporation of white liquor to drop out NaCl, electrolysis of NaCl, HCl formation, and ClO_2 generation by the hydrochloric acid process.

Incineration of holopulp spent liquor has been studied in some detail. When the amount of chlorine in the spent liquor is less than about 1/4 the sodium on a mole basis, a conventional soda furnace can be used. The major unknowns are the amount of dust carryover to be expected and the upper limit of the chlorine content which can be tolerated. Pilot-scale testing would be needed to define these factors and gain a greater degree of confidence in the approach.

Fluidized bed incineration is not feasible when the liquor composition is such that the ash contains more than 1% Na_2CO_3. It does appear workable when a slight excess of chlorine is present in the liquor so that Na_2CO_3 formation is prevented. In this event it would be necessary to scrub a small amount of HCl from the flue gas. Extensive pilot testing would probably be required before this approach would be ready to go commercial.

Studies on chemical recovery for holopulp appear to have reached a point of diminishing returns until there is a significant increase in scale. Remaining questions regarding incineration, evaporation, and purity of recovered chemicals cannot be adequately answered without pilot tests using relatively large quantities of actual spent pulping liquor.

INTRODUCTION

Chemical recovery in the holopulping process was first discussed in Report Five (1) in which the major elements of a recovery system were outlined. The system was analyzed in detail in Report Eleven (2) and the areas of greatest uncertainty identified. Report Fifteen (3) presented the results of laboratory work which supported the validity of the recovery concepts. Larger scale tests of the feasibility of fluidized bed incineration of the spent liquor were described in Report Seventeen. Based on this background, this report is intended as a summary of the present status of chemical recovery systems for the holopulping process.

The basic requirements for a chemical recovery system are set by the pulping conditions employed. Holopulping may be considered to consist of a range of processes broadly delineated by thermomechanical defibration of wood chips along with sequential steps involving the use of caustic and oxidative treatments based mainly on the use of chlorine dioxide, chlorine, and hypochlorite. Under these conditions, the pulping chemicals can be considered to consist of ClO_2, Cl_2, and NaOH. The spent liquor will then contain sodium and chlorine as the principal inorganic constituents. Thus, the chemical recovery system is required to process an effluent containing dissolved organics along with sodium and chlorine, and regenerate the necessary pulping chemicals, ClO_2, Cl_2, and NaOH.

It is possible to expand the general concept of holopulping to include chemical pretreatments by conventional processes such as kraft or sulfite prior to (or concurrent with) chip defibration. The general effect of such a procedure would be to introduce sulfur into the spent liquor, and hence into the recovery

system. It has been the practice in this project to confine attention to "sulfur-free" systems, and all of the work on recovery which has been done has been with sulfur-free systems. Accordingly, this report will be generally restricted to the chlorine dioxide (and chlorine)-alkali processes discussed above.

BASIC RECOVERY CONCEPTS

Holopulp chemical recovery involves two key steps; combustion of the organic material in the spent liquor, and regeneration of the pulping chemicals from the inorganic combustion products. Both of these steps are strongly influenced by the relative amounts of sodium and chlorine in the spent liquor.

Combustion is the only practical method for separating the sodium and chlorine from the organic material and for destroying the organic. This step is basic to the entire recovery process. The combustion step would normally be preceded by concentration of the liquor. The extent of concentration required would be dependent on the type of combustion system employed. It appears that evaporation of the spent liquor is the best method presently available for achieving the necessary concentration.

The combustion products formed are dependent on the molar ratio of sodium and chlorine in the spent liquor. At a molar ratio, Na/Cl, of 1, sodium chloride would be the only significant combustion product. If there is an excess of sodium (Na/Cl > 1), that sodium which is not tied up as sodium chloride would be converted to carbonate, Na_2CO_3. If chlorine is present in excess (Na/Cl < 1), the combustion products will be hydrogen chloride (HCl) and NaCl. The formation of these products is not appreciably influenced by whether or not oxidizing or reducing conditions are maintained, so long as chemical equilibrium is approached.

Regeneration will involve the electrolysis of the NaCl to form caustic, Cl_2 and H_2. Electrolysis is the only method for producing NaOH and Cl_2 from NaCl which is currently practical. Since the sodium in the recovered NaCl derives from the NaOH used in pulping, the use of electrolytic chlor-alkali cells in a closed recovery system is mandatory.

The Na_2CO_3 which is formed when an excess of sodium is present can be causticized with lime in a more or less conventional fashion. Whether or not it is practical to do this depends on the relative amounts of Na_2CO_3 and NaCl which are present. If causticizing is employed, it would be done on the NaCl-Na_2CO_3 mixture. The resulting white liquor would then be concentrated to drop out the NaCl for subsequent electrolysis. If causticizing is not used, the Na_2CO_3 would be reacted with HCl to convert it to NaCl for electrolysis.

A good many systems for generating ClO_2 are in commercial use. All of these employ a reaction between sodium chlorate and a reducing agent under strongly acidic conditions. They differ in the type of reducing agent and acid employed and consequently in the type and amount of ClO_2 generator effluent produced. Most of these processes employ sulfuric acid and generate H_2SO_4 and/or Na_2SO_4 as by-products. In a closed, sulfur-free process, such effluents would have no internal use and their disposal would be a burden to the process. Consequently, the only ClO_2 generation processes which are suitable for holopulping are those which involve hydrochloric acid. The reaction can be written as follows:

$$NaClO_3 + 2HCl = ClO_2 + \frac{1}{2} Cl_2 + NaCl + H_2O$$

The NaCl which is formed in this reaction can be sent to electrolytic cells to regenerate the chlorate according to the reaction:

$$NaCl + 3H_2O + 6 \text{ faradays} = NaClO_3 + 3H_2$$

Processes which employ these reactions with on-site chlorate production are commonly called Kesting processes. The overall reaction can be represented as:

$$2HCl + 2\ H_2O + 6 \text{ faradays} = ClO_2 + \frac{1}{2} Cl_2 + 3H_2$$

The chlorine which is formed can be separated from the ClO_2 and burned with hydrogen to form a part of the HCl needed. The remainder of the HCl is obtained by burning the chlorine from the chlor-alkali cells with hydrogen.

When a significant excess of chlorine exists in the spent liquor, HCl could be scrubbed directly from the combustion gases. It is quite conceivable that this HCl could be concentrated and fed directly to the ClO_2 generator.

The use of electrolytic chlor-alkali cells in the regeneration step places some rather severe limitations on the use of sulfur in the pulping operation. Under the oxidizing conditions which would be used in the incineration step, this sulfur would be converted to Na_2SO_4. Sodium sulfate can be very detrimental to cell operation and must be kept to low concentrations. Thus, it would have to be purged from the system. Precipitation with barium carbonate or other removal methods can be expensive, and also constitute a disposal problem.

The chemistry of the holopulp recovery system can be summarized by the following reactions:

$$ClO_2 + Cl_2 + NaOH + \text{wood} \rightarrow \text{spent liquor (Na, Cl)}$$

$$\text{spent liquor (Na, Cl)} \xrightarrow{\text{combustion}} NaCl + Na_2CO_3 \text{ or } HCl$$

$$NaCl + H_2O + 1 \text{ faraday} \rightarrow NaOH + \frac{1}{2} Cl_2 + \frac{1}{2} H_2$$

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3$$

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

$$\frac{1}{2} H_2 + \frac{1}{2} Cl_2 \rightarrow HCl$$

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

and $$2HCl + 2H_2O + 6 \text{ faraday} \rightarrow ClO_2 + \frac{1}{2} Cl_2 + 3H_2.$$

SYSTEM CONFIGURATIONS

These basic concepts can be employed to develop a number of different systems depending on the ratio of sodium to chlorine in the spent liquor and on the degree of closure of the system. Basically, it is possible to consider four general systems for holopulp recovery:

1. A recovery system in which <u>all</u> regeneration involves electrolytic processes.
2. A recovery system involving causticizing of Na_2CO_3 as well as electrolysis of NaCl.
3. A system in which a kraft recovery system is used for incineration of the liquor.
4. A totally open loop system.

These are shown in diagram form in Fig. 1 through 4.

The first system would be employed when there would be relatively little Na_2CO_3 in the recovered ash. In this situation, the complexity of separate causticizing of the Na_2CO_3 is not justified and a portion of the HCl would be recycled to convert the Na_2CO_3 to NaCl for electrolysis. In this situation, all of the NaOH used in the pulping step would be electrolytically produced.

The second system would be used when there is sufficient Na_2CO_3 present to justify a separate causticizing system. All of the recovered ash would be

Diagram of "All-Electrolytic" Holopulp Process

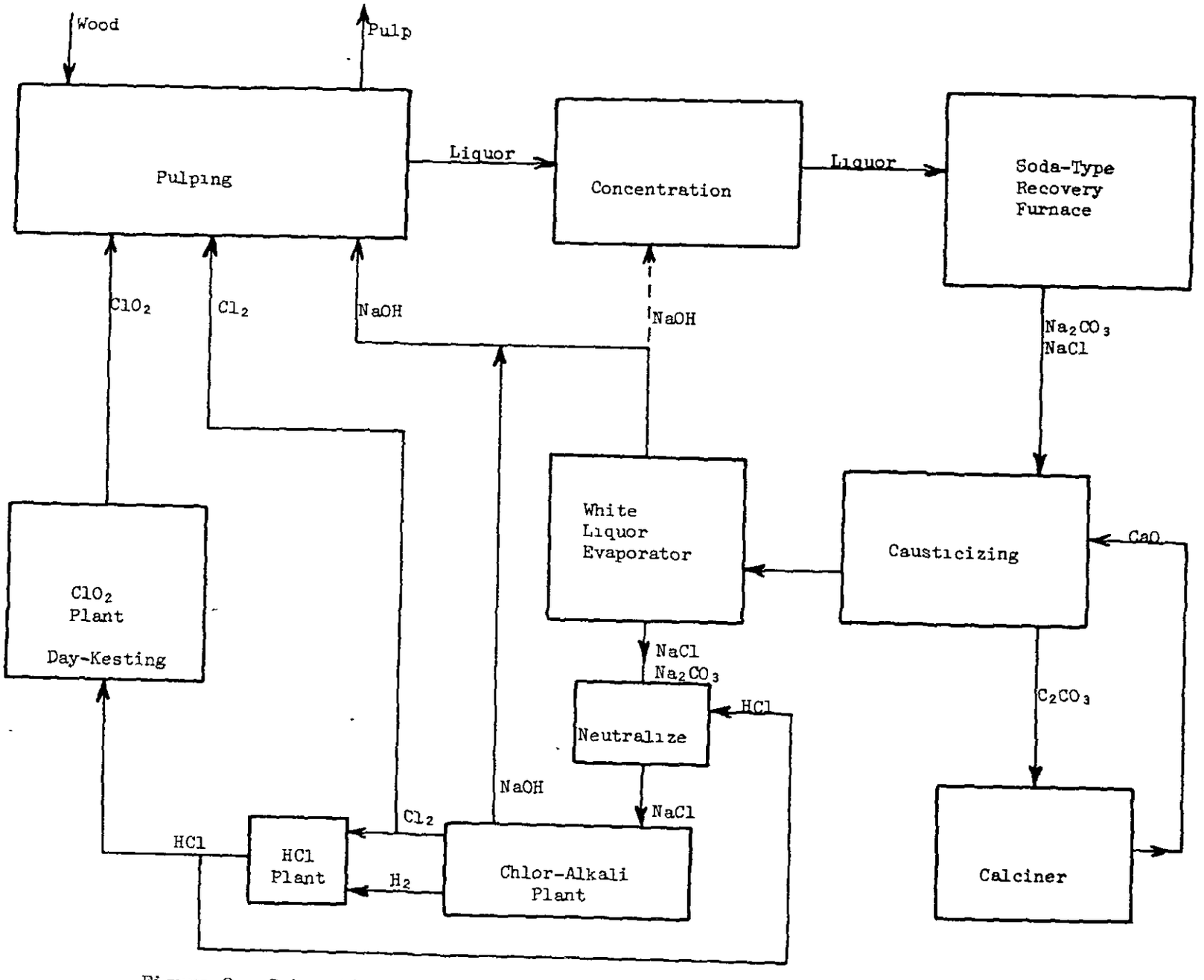

Figure 2. Schematic Diagram of Holopulp Process Employing Causticizing

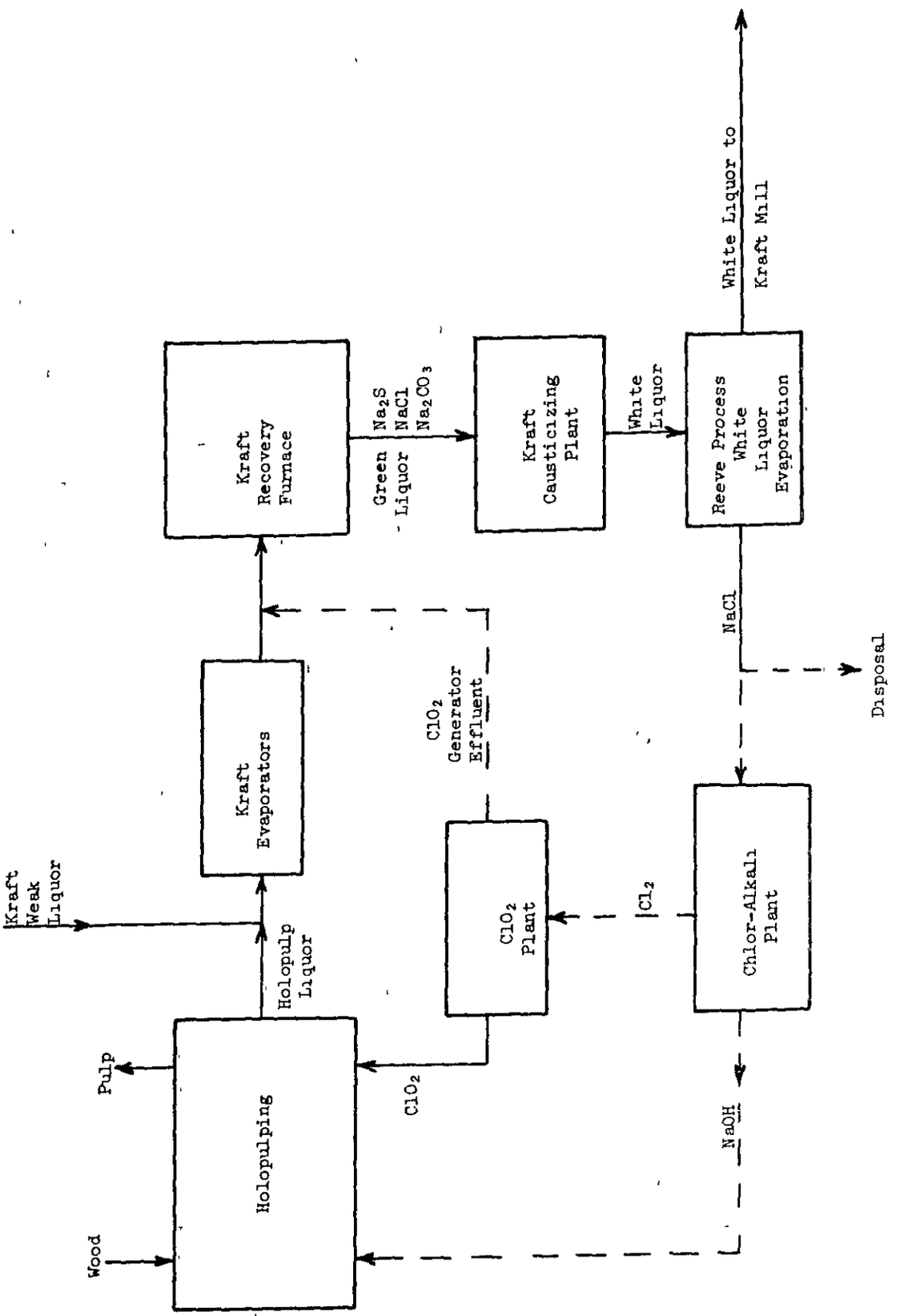

Figure 3. Schematic Diagram of Cross-Recovery with Kraft

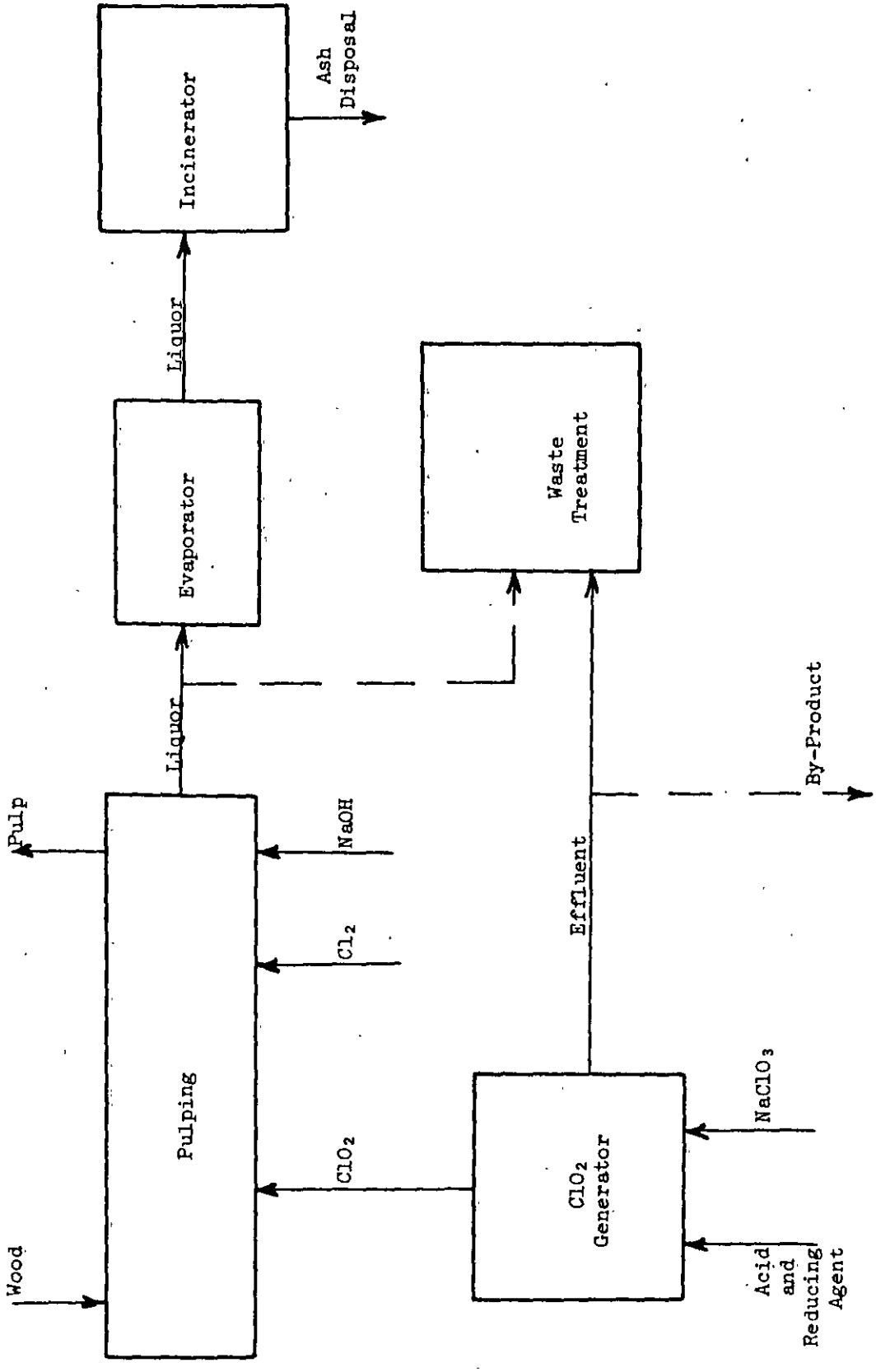

Figure 4. Schematic Diagram of Open-Loop System

sent through the causticizing system. The NaCl would then be separated from the NaOH by concentration of the white liquor. This NaCl would then be electrolyzed. In this system, a part of the NaOH needed for pulping would be produced non-electrolytically, and the size of the chlor-alkali plant would be determined by the amount of chlorine used (as ClO_2 or Cl_2) in pulping.

Under certain circumstances, it could be advantageous to run a small holopulp operation in a sort of cross-recovery with a kraft system. The holopulp liquor could be added to the kraft liquor system and evaporated and burned. The main effect on the kraft system would be the introduction of chlorine which would be converted to NaCl in the kraft furnace. This NaCl could then be removed by white liquor evaporation and either electrolyzed or disposed of. One advantage of such a procedure is that it would permit the use of some sulfur in the holopulp process.

A final possibility is to operate the holopulp process so as to provide only for treatment of the effluents without effective recovery. This would probably involve concentration and incineration of the spent liquor and disposal of the ash, and some means for treating or otherwise disposing of the ClO_2 generator effluent. One advantage of this approach would be to eliminate the costs for the on-site electrolytic plants. This advantage is only apparent, however, since it would merely shift the costs to off-site electrolysis borne by the chemical supplier. This system would also permit the use of sulfur in the pulping operation.

EVAPORATION AND INCINERATION

From the beginning of the work on recovery for holopulp it was recognized that evaporation and incineration of the spent liquor were the steps furthest removed from existing technology. The regeneration steps generally involved proven technology (at least at the pilot plant level) and the major questions in those areas lay with the purity of the recovered chemicals. Combustion of the spent liquor was generally considered to be the key operation, and most of the work on recovery has focussed on it.

Preliminary work on evaporation and combustion of holopulp liquor was presented in Report Fifteen (3). Evaporation was carried out up to about 25% solids. It was shown that the chlorine compounds present in the liquor were nonvolatile and remained with the concentrated liquor. On the other hand, volatile organics, such as methanol, were carried over and the condensate did have a significant BOD loading. No serious problems were encountered in carrying out those evaporations.

The work on combustion centered on studies of the equilibrium behavior of sodium-chlorine systems, the nature of the combustion products, the general combustibility of the liquor, and the potential air emission problems which might exist. Thermodynamic equilibrium calculations clearly indicated that the only significant combustion products would be NaCl and either Na_2CO_3 or HCl depending on whether sodium or chlorine was present in excess. Laboratory combustion experiments confirmed these predictions. The heating values of the liquors tended to run 15 to 25% below kraft values but were high enough to support combustion without auxiliary fuel in a properly designed furnace.

It was recognized that NaCl was quite volatile and that very high fume loadings could be involved. This appeared to be the only significant air emission problem unless chlorine was present in excess.

Several combustion concepts appeared to be applicable to holopulp recovery. These included fluidized bed incineration, incineration in a more or less conventional recovery furnace, and wet combustion (Zimmermann process). Each of these were investigated in some detail in the most recent phase of this study.

FLUIDIZED BED COMBUSTION

There are several process advantages to the use of fluidized bed incineration in holopulp recovery. Equilibrium calculations indicate that air emissions are lower at lower temperatures. This is especially true of NaCl volatilization and subsequent fume generation. Fluidized bed incineration is carried out at temperatures below the melting point of the ash so that smelt-water explosion hazards are eliminated. A fluidized bed furnace would permit significant savings in capital compared to a conventional recovery furnace. It could also decrease evaporator requirements since indirect evaporators would be needed only to raise the solids content to about 30% solids. A direct contact evaporator-scrubber could then be used to achieve firing concentrations. It is recognized that fluidized bed incineration is less satisfactory from an energy recovery standpoint than a conventional recovery furnace; however, it appears that the advantages of fluidized bed incineration could outweigh the penalties.

Initial work on fluidized bed incineration of holopulp spent liquor was carried out at the Institute and described in Report Fifteen (3). It was recognized that NaCl and Na_2CO_3 form a eutectic at 44% NaCl and 56% Na_2CO_3

which melts at about 1175°F. and that this temperature was too low for successful incineration. However, melting point tests indicated melting points above 1400°F. for ash compositions greater than 60% NaCl, and it appeared that fluidized bed combustion might be possible in this region. Attempts to verify this on a six-inch diameter bed were plagued with experimental difficulties and were inconclusive.

Dorr-Oliver Tests

The next step involved two test runs carried out at Dorr-Oliver. These tests were described in detail in Report Seventeen (4). The objective of these tests was to determine the feasibility of fluidized bed incineration of a liquor producing a Na_2CO_3-NaCl ash, in the face of the low melting eutectic. A synthetic holopulp liquor, prepared by adding hydrochloric acid to a soda process spent liquor, was used in these tests.

The first test was designed to examine the behavior when the ash composition was very close to 100% NaCl (very little eutectic present). Hydrochloric acid was added to the soda liquor so that some HCl was found in the flue gas. Then a small portion of soda liquor was blended back in until no HCl carryover was observed. This "balanced" liquor was used for the remainder of the test. The bed was held at 1200°F. for most of the test run. This run was plagued by troubles with the liquor feed pump. When it became apparent that operation could not be sustained, the bed temperature was raised to try to determine the defluidization temperature. The bed defluidized at a temperature between 1250 and 1280°F. Analysis of the fused material showed 97-98% NaCl and 1 to 1.3% Na_2CO_3.

In the second test, the proportion of sodium to chlorine in the liquor was adjusted to give a small excess of sodium. Chlorine gas was then injected directly into the bed with the rate of addition just below that at which HCl appeared in the stack gas. This was an attempt to dynamically balance the Na and Cl content of the ash. The bed temperature was kept between 1160 and 1200°F. and after 15 hours, the fluidization became progressively more sluggish and the test was terminated. Analysis of the bed material after shutdown showed NaCl contents of about 95% and Na_2CO_3 contents of 1.4%.

It was concluded that fluidized bed incineration of these liquors could not be maintained under conditions in which HCl was absent from the flue gas. As little as 1 to 1.5% Na_2CO_3 in the bed was sufficient to cause tackiness and eventual fusion of the bed. Thus, fluidized bed incineration of holopulp liquor is essentially limited to those cases in which chlorine is present in excess of sodium in the liquor being fired.

Despite the negative results on fluid bed, some aspects of the Dorr-Oliver tests were encouraging. The combustion products followed thermodynamic predictions rather closely. There were no significant air emissions except for HCl when the chlorine content of the liquor approached or exceeded a 1:1 ratio with sodium. No chlorine was detected in the flue gas, even when gaseous chlorine was injected into the bed.

Discussion with Others

After completion of the tests at Dorr-Oliver, contacts were made with other people active in fluidized bed incineration. These included Chicago Bridge and Iron Company, Copeland Systems Inc., and Prof. Arthur Squires of the City College of the City University of New York. The objective of these contacts was two-fold:

1. To determine if there was any reason that the conclusions developed from the Dorr-Oliver tests (namely that fluidized bed combustion was not feasible if the Na_2CO_3 content of the ash exceeded about 1 to 2%) were erroneous.
2. To determine if there was any reason why fluidized bed incineration of a liquor containing an excess of chlorine would not work.

The most fruitful discussions were held with Chicago Bridge and Iron Company, who have a substantial background in fluid bed combustion of pulping liquors. Most of their work was with sodium-base liquors from neutral sulfite pulping in which chloride entered as a contaminant. They found that they got into trouble when the chloride content reached a level equivalent to 1% NaCl on the ash. The effective fusion temperature of the ash showed a very rapid drop of about 150 to 200°C. at about the 1% NaCl level. The steepness of the drop was considered as indicative of a "critical" NaCl concentration being reached. From the nature of eutectics they expected a similar behavior would be exhibited on the chloride rich end and were not at all surprised that 1 to 2% Na_2CO_3 in an NaCl bed led to defluidization.

They had had some success in overcoming the ash sticking problem in Na_2SO_4-Na_2CO_3 beds containing 1% NaCl, by adding lime. It was necessary to add 6 to 8 times the "stoichiometric" amount of lime before the fusion point was raised significantly. The behavior followed an S curve with a flat fusion temperature vs. lime addition until a critical amount was added whereupon the effective fusion temperature rose rapidly to the Na_2SO_4-Na_2CO_3 fusion point. They were not sure why this worked. It may have been purely a diluent effect or

it may have been an actual change in the chemistry of the eutectic. They did not experiment with a lot of other materials than lime.

It was concluded that lime addition was not the answer to our problem. It would only be effective if small quantities of the eutectic forming substance (Na_2CO_3 in our case) were present, since otherwise massive lime addition would be needed. When it is considered that typical holopulp conditions would lead to an ash containing at least 20% Na_2CO_3, a major adjustment in Cl_2-ClO_2 consumptions or extensive HCl addition would be required to give a 1 to 2% Na_2CO_3 ash where lime addition might be feasible. Having gone that far it would seem to be more appropriate to go to an excess of chlorine so that the eutectic is totally eliminated.

They were quite confident that fluidized bed combustion could be carried out in NaCl beds provided they were Na_2CO_3 free, and indicated that they had done it. They have carried out a successful test run on their 24-inch diameter pilot bed on a chlorinated hydrocarbon waste stream from a refinery. In this case, NaOH was added to the stream before incinerating it to provide an NaCl ash. They also successfullv carried out a test on bleach effluent (no details on how this was prepared were given), which gave an ash which tested out 96% NaCl and no Na_2CO_3.

They did not believe it was feasible to operate at temperatures below the Na_2CO_3-NaCl eutectic temperature even if we were willing to accept large amounts of unburned carbon in the ash. The reason is that combustion rates become so low below about 1200 to 1250°F. that the stability of the system becomes a problem.

On the basis of the discussion with Chicago Bridge and Iron Company, the following conclusions could be drawn:

1. The conclusions drawn from the Dorr-Oliver tests were correct. Fluidized bed incineration of holopulp liquor is not feasible when the Na_2CO_3 content of the ash exceeds 1 to 2%.
2. There is every likelihood that operation with an excess of chlorine in the liquor would be successful provided the HCl scrubbing problem could be handled.
3. It is possible that fluidized bed incineration without significant HCl emissions would be feasible provided that the liquor can be stoichiometrically balanced so that the Na_2CO_3 content of the ash is less than 1%.

A meeting was also held with Copeland Systems Inc. These discussions never did touch significantly on technical matters and were concerned primarily with the need to protect Copeland's know-how. A list of conditions which Copeland felt necessary for their cooperation was considered unacceptable and the matter was not pursued further.

A contact was also made with Prof. Arthur M. Squires who is Principal Investigator of the City College Coal Research Team. They are interested in coal gasification technology and have been undertaking studies of fast fluidized beds and agglomerating fluidized beds. This involves a developing technology in which space velocities significantly higher than those employed in conventional fluidized beds are used. Particular advantages with "sticky" particles can be obtained by using larger size particles and higher velocities. These concepts are discussed in some detail in Reference (5). Although this work is not directly

applicable to the holopulp incineration problem, it seems to indicate that there could be advantages to operating at higher fluidizing velocities in the sluggish region, and that developing technologies could provide an alternative for hololiquor incineration.

IPC Tests

In order to verify the tentative conclusion that fluidized bed incineration of a liquor containing an excess of chlorine was feasible, it was felt to be necessary to carry out a test with such a liquor. An inquiry was made to Dorr-Oliver. They refused to run the test because of corrosion problems which had developed on their old test system after our previous runs. An inquiry to Chicago Bridge and Iron also met with refusal because incineration of pulping liquors is outside of their current range of interest. Accordingly, it was decided to rebuild our fluidized bed furnace and carry out the tests at the Institute.

Details of the fluidized bed test facility, the preparation of the liquor, and the test runs are given in Appendices I, II, and III, respectively.

Tests were carried out with an actual holopulp liquor to which sufficient hydrochloric acid was added so that the amount of chlorine in the liquor was 2% in excess of that needed to convert all sodium to NaCl.

The first run was carried out at a bed temperature of 1180°F. and a superficial velocity of 2.5 ft./sec. This system operated quite well for a period of about five hours with a carbon burnup rate (based on CO_2 in the flue gas) of 82%. After this time, the bed defluidized. By poking the bed with a rod and increasing the fluidizing velocity to 3.1 ft./sec., it was possible to refluidize the bed. It was then kept going for another three hours at a bed

temperature of 1150°F. and a carbon burnup of about 70%. At this point, the bed again defluidized and the run was terminated.

The second run was carried out at a fluidizing velocity of 3.1 ft./sec. and a bed temperature of 1215°F. This system operated flawlessly for about a four-hour period with a carbon burnup rate of 95%. At this time, it began to show signs of incipient defluidization and the fluidizing velocity was gradually raised over a three and one half hour period finally reaching 3.9 ft./sec. At this point, the system was so sluggish that it was shut down.

In both cases, there was no evidence of fusion (extensive melting and resolidification) of the bed material. The defluidized beds were rather easily knocked apart and broken up into free flowing particles. The bulk of the individual particles in the defluidized beds was significantly greater in size than the original starting bed material. Clearly this system forms an agglomerative bed with the size of the individual particles continually growing. In the test system used here, there was no provision for removing oversize bed material during operation except for an occasional entrained particle. Thus, the particles would eventually grow to a size where they could no longer be fluidized at the prevailing velocity and bed defluidization occurred. Thus, there does not appear to be any inherent reason why fluidized bed incineration could not be used with these liquors. All that would be necessary to sustain operation would be a method for continually removing an amount of large particles and possibly reseeding the bed with smaller particles. The defluidization which occurred in these tests appears to be an artifact of the test facility.

On the basis of these tests, the use of fluidized bed incineration on spent liquors containing an excess of chlorine appears quite promising. The only restriction is that bed temperatures in these tests have been slightly

lower than the values generally considered desirable for pulping liquor combustion. Plans are underway to carry out additional tests after slight modifications of the system.

Status of Fluidized Bed Incineration

The present status of fluidized bed incineration in holopulp recovery is that it does seem to have a place in systems in which the Na/Cl ratio is close to 1. Fluidized bed incineration is not feasible when the Na_2CO_3 content of the ash exceeds about 1 to 2% (Na/Cl > 1.01). However, it does appear very promising when there is an excess of chlorine present in the liquor provided the small amount of HCl can be scrubbed from the flue gas. This would appear to be primarily a materials problem.

There appear to be no difficulties in integrating the fluid bed furnace into the rest of the system. The recovered solids can be sent directly to the brine purification system for the chlor-alkali plant. The weak acid from the HCl scrubber could be used as make-up water for the strong acid towers following the H_2-Cl_2 burners. The only uncertainty is the possible build-up of impurities in the recycling of chemicals which could bring new eutectics into play.

CONVENTIONAL RECOVERY FURNACE

Investigation of the feasibility of using conventional recovery furnaces proceeded in conjunction with The Babcock & Wilcox Company. This study included obtaining certain physical property and combustibility data on holopulp spent liquors and calculations with a computer model for the furnace. This information, along with their experience, was used to examine the problems involved in the

evaporation and burning of holopulp spent liquor and to make some preliminary judgments on the feasibility of several incineration approaches.

Two liquor samples, A and B, were sent to B & W. Both were made from hardwoods, with Liquor A containing a higher proporation of chlorine (Cl:Na = 0.75) than Liquor B (0.38). Data obtained on these liquors included elemental analyses, heating values, trace metals, viscosities, and thermogravimetric analyses. In addition, the behavior during concentration was observed. Details of the preparation of the liquor samples and summaries of the data obtained are given in Appendix IV.

Liquor concentration was carried out at 160°F. in a rotary vacuum evaporator. B & W's work on the volatilization of chlorine compounds essentially paralleled our earlier work. There was no odor of chlorine or any other identifiable compound and the evaporator condensates were clear and odor free. A chlorine material balance appears to show a slight loss of chlorine on evaporation of the liquor, but these may well be within the accuracy of the chlorine determination. Direct analysis of the condensate and caustic scrubber for the noncondensible showed very little chloride present. They did note that evaporation of water from the holopulp liquors was much slower than it is for kraft liquors. This is apparently associated with the high viscosity characteristics of the holopulp liquor.

Their tests showed the holopulp liquors to be substantially more viscous than kraft liquors at high solids levels. The difference could be as much as one or two orders of magnitude. Viscosities this high would make it difficult to concentrate the liquors to high solids and could cause problems in handling the liquor. The liquors were definitely non-Newtonian in behavior, with the

viscosity decreasing with increasing shear rate. Liquor A was found to be extremely foaming under shear at temperatures above 185°F. This is unusual, since foaming problems had not previously been encountered with holopulp liquors, and none were observed with Liquor B. The fact that the liquors were stored for five months before the tests were run may have had an influence on this behavior.

Because of the severity of the viscosity behavior, the problem was examined further at the Institute. This followup work is described in Appendix V. This work confirmed the high viscosities of holopulp liquors as they are initially prepared. It also showed that pH plays a dominant role in the viscosity behavior. The viscosity of the liquor could be dropped by more than an order of magnitude by raising the pH to > 12.2. Similar behavior is observed at the low pH end. It appears that the intermediate range of liquor pH values is the worst from a viscosity standpoint.

It is of interest to note that in the preparation of the liquor for the fluidized bed test runs (Appendix II), the liquor was concentrated in a forced circulation evaporator to about 52% solids without difficulty. This was carried out in the intermediate pH range. After acidification with HCl, this liquor became very free flowing.

The thermogravimetric analyses that were run by B & W showed the combustibility of holopulp liquors to be equivalent or slightly better than kraft. There is no question that this liquor will burn. The problem is to find the most effective way to carry it out.

Computer simulations of the firing of holopulp liquors were run to obtain some idea of how they might behave in a kraft furnace. In spite of their relatively low heating values, the model-predicted bed temperatures are above

the normal kraft range. This is apparently due to the absence of sulfate reduction which normally absorbs substantial heat in the kraft furnace. The result of the high bed temperatures and the greater volatility of the holopulp ash is a very high carryover and relatively little smelt formation. The computer model predicted very high dust loads at all of the conditions tested. Subsequent to the work done on holopulp, the model was tested on its ability to predict dust loadings for a soda furnace. The predictions were comparable with operating experience and thus there is some support for the validity of the dust loadings predicted for holopulp. However, the holopulp calculations were not run at primary air levels quite as low as those used in soda liquor incineration, so the holopulp estimates may still be excessive.

After the tests were completed and reported, a meeting was held with research and operating people from B & W to discuss the problems of holopulp liquor combustion. It was generally felt that a liquor containing a high proportion of sodium (nominal ash content of 25% NaCl and 75% Na_2CO_3) could be burned in a recovery furnace similar to those used for incineration of soda liquors, provided the liquor could be concentrated to 60-65% solids. This consensus was based on their experience with soda recovery boilers and with kraft mills with high chloride contents. They felt that we could probably get away with a heating value as low as 5000 Btu/lb. solids without the need for support fuel. The biggest uncertainty appears to lie with the extent of dust loadings which would be involved (and thus with the precipitator size). The construction of the furnace would not be appreciably different from a conventional furnace. The only concession they make in designing for a high-chloride kraft furnace is to specify a slightly lower temperature (1200°F. instead of 1300°F.) entering the tube banks (which makes the furnace a little bigger). They do not space the tubes wider or use different materials.

Based on these discussions, the following conclusions can be drawn:

1. There is a very high probability that a holopulp liquor, in which sodium is predominant, can be burned in a conventional soda recovery furnace. This is strongly indicated for NaCl contents up to 25% on the ash, and may be valid at much higher NaCl levels.
2. The capital cost of the recovery furnace itself should not be significantly greater than that for a conventional furnace of comparable Btu rating.
3. The cost of the precipitator could be significantly higher depending on fume loading and particle characteristics. The extent of carryover during the combustion of holopulp spent liquor is probably the biggest unknown at the present time.
4. Use of the conventional recovery furnace is contingent upon the ability to concentrate the liquor to 60-65% solids. Going to high solids without overcoming the viscosity problem could involve new technology and would likely stretch out development time and costs.

The above conclusions are about as far as it is possible to go at the current scale of effort. They would have to remain somewhat tentative until backed up by actual test firing of holopulp spent liquor in a pilot furnace. A preliminary estimate of the costs and requirements for such a test program was made by B & W. The program would cost about $125,000, take from six to nine months to complete and would require a minimum of 30,000 gallons of waste liquor at 45% solids.

WET COMBUSTION

Wet combustion (Zimmermann process) was another process which appeared to have applicability to the holopulp chemical recovery problem. In this process, the liquor is contacted with air at temperatures of 500 to 700°F. under pressures (up to 3000 p.s.i.) which maintain the liquid phase. Under these conditions, the organic materials are oxidized and the inorganics remain in solution from which the cooking chemicals can be regenerated.

There appeared to be several significant advantages to this process if it could be applied. It could eliminate the evaporators and hence any problems with noncondensible gases or evaporator condensates. It would also eliminate potential HCl emissions during combustion. There was a possibility that the capital costs for the Zimmermann process would compare favorably with costs for an evaporator, recovery furnace, and precipitator.

It was recognized that there were two major problems which might limit the applicability of wet combustion to the holopulping process:

1. Since the solution from the wet combustion step would be subject to electrolysis, it was necessary to get very complete oxidations with a minimum of residual chemicals in the product liquor.
2. There was a major materials problem due to the corrodibility of chlorides at the temperature levels which would be required. Even titanium would not be effective unless the system was acidic.

A sample of holopulp liquor was sent to Zimpro Inc. for tests on the applicability of wet oxidation. This liquor was one in which the amounts of sodium and chlorine were substantially in balance, since this was considered

to be the most favorable from a materials standpoint. It was subjected to wet oxidation in a titanium autoclave. No major corrosion problems occurred. They were able to achieve a 93.5% reduction in the COD of the liquor. A small sample of the oxidized liquor was returned for analysis. The liquor was quite brown in color. This color was identified as being due to lignin reaction products similar to those which are responsible for the color of bleach effluents.

Because of the relatively high amount of residual organics in the treated liquor (apparently more than they normally get) serious reservations existed about the ability to electrolyze it. There appeared to be only two possibilities for using wet combustion.

1. Carry out the wet combustion to the point of complete destruction of the organic constituents.
2. Concentrate the oxidized liquor in a crystallizer-evaporator to obtain NaCl crystals for subsequent analysis.

The first alternative is of course, dependent on the ability to use more extensive oxidizing conditions. The second is not attractive because the amount of evaporation needed would be comparable in magnitude to the evaporation of the original liquor and, thus, one of the main advantages of wet oxidation would be lost. Use of wet oxidation on high sodium liquors (in which causticizing of the reaction product would be employed) did not look attractive from a materials standpoint.

These points were brought up with representatives of Zimpro. They agreed that wet oxidation did not look promising for holopulp recovery. They stated that there was no way to get complete oxidation and that some residual organics would be present. Furthermore, the materials of construction problem

was horrendous and they were not at all certain they could contain the liquor under the reaction conditions. Consequently, they saw no hope for Zimpro in this application.

SUMMARY

There are two incineration concepts which appear to be applicable to combustion of holopulp liquor on the basis of the small scale studies which have been carried out to date. Each of these appears to be most suitable for certain ranges of Na/Cl ratio in the spent liquor. They are as follows:

1. For systems in which Na/Cl is about 3 to 4, a conventional soda-type recovery furnace could be used. This would require liquor concentrated to 60-65% solids and probably an enlarged precipitator to handle increased particulate loads.
2. For systems in which Na/Cl is close to 1, fluidized bed incineration should be possible. This would require the addition of some HCl to the liquor to ensure an excess of chlorine during combustion and the need to scrub small amounts of HCl from the flue gas.

The first approach is a straight extrapolation from present technology. The major unknowns are the amount of dust carryover to be expected and the upper limit of the chloride content which can be tolerated. Pilot-scale testing would be required to gain a greater degree of confidence in this approach. This would cover the following points:

1. Assess the capability to maintain stable combustion without auxiliary fuel.

2. Assess the capability to limit inorganic carryover as fume.
3. Assess the possibility of NaCl enrichment in the fume relative to the smelt.
4. Assess the tendency for HCl to occur in the flue gas.
5. Examine the upper limits of tolerable chloride levels.

The second approach also appears to be rather soundly based, although it may be slightly more removed from present technology. The evidence pointing to the success of the approach appears reasonable. This includes successful pilot tests by Chicago Bridge and Iron on NaCl beds as well as the work carried out on our own facility. Scrubbing HCl from the flue gas could be a nuisance, but it would not seem to involve any major technical problems. It is possible that techniques for continual control of the Na/Cl balance could be developed which would eliminate the need for excess chlorine and hence HCl emissions. Extensive pilot testing would probably be required before this approach would be ready to go commercial. Such items as the best way to control particle size, reaction conditions, type of HCl scrubbing system, etc., would need to be examined.

Although there are indications of a potential viscosity problem with holopulp liquors, this should not seriously inhibit the ability to concentrate the liquor. The viscositv of the liquors is highest at intermediate pH levels, while the incineration concepts themselves require Na/Cl ratios which are characteristic of quite alkaline and acid liquors, respectively. Thus, if viscosity does become a problem, recycled NaOH or HCl can be added to the liquor prior to critical concentration steps. Besides this, the liquors are quite non-Newtonian and an intermediate pH liquor was concentrated to high solids in a

forced-circulation evaporator quite easily. Aside from the viscosity problem, evaporation is well behaved. Chlorine compounds have proved to be nonvolatile and remain with the liquor. However, BOD levels in the condensate are higher than they are in the kraft process.

REGENERATION

The regeneration of the pulping chemicals from the combustion products NaCl and Na_2CO_3 is straightforward and involves available technology. Accordingly, very little work has been devoted to this aspect of the recovery problem on this project. However, since this report is intended to summarize the current status of the holopulp recovery system, it is appropriate to review these operations. The following are the major concepts involved in the regeneration system.

1. All of the NaCl which is recovered is converted to NaOH, Cl_2 and H_2 by electrolysis in chlor-alkali cells.
2. The Na_2CO_3 which is recovered may be causticized with lime. This would be followed by white liquor concentration to drop out the NaCl for electrolysis.
3. Alternatively the Na_2CO_3 may be reacted with HCl to form NaCl which is then electrolyzed.
4. ClO_2 is generated from Kesting-type processes which include on-site chlorate generation and the use of hydrochloric acid.
5. Any HCl needed is formed by reaction of H_2 with Cl_2.

ELECTROLYTIC PROCESSES

Holopulping can be looked upon as an electrolytic pulping process, since the pulping chemicals are all produced electrolytically. Two types of electrolytic cells are involved, chlor-alkali cells for production of Cl_2 and NaOH, and chlorate cells which are involved in ClO_2 production. Production of HCl by burning Cl_2 in H_2 is a closely related operation.

Chlor-Alkali Plant

Electrolysis of brine to produce caustic and chlorine is a well-established technology which could be readily adapted to holopulp recovery. Either diaphragm cells or mercury cells could be used as the basis for chlor-alkali production. There are no inherent limitations to either of these methods. The choice of which system to use can be deferred until after pilot plant tests on more critical aspects of the holopulping process have been completed.

Although new technical developments in chlor-alkali production are occurring, they are unlikely to influence the feasibility of holopulp recovery or the configuration of the recovery system. At present, there is much interest in metal electrodes or dimensionally stable electrodes. While these may be a definite improvement, they are unlikely to result in a major breakthrough in costs or performance, and hence would have relatively little impact on the holopulp system. The success or failure of holopulp recovery is not dependent on technological developments in this area.

The major uncertainty in the chlor-alkali area lies with the possible contaminants in the recovered salt and the resultant demands on the brine purification system. Calcium, magnesium, sulfate, and heavy metals are among the possible contaminants which could cause trouble. No work along these lines has been carried out to date because it was felt that the ash from small combustion experiments was not representative of the real system. Meaningful answers to the brine purity question would have to await larger scale pilot incineration tests of large quantities of actual holopulp spent liquors.

ClO_2 Production

The major constraint on ClO_2 production in a closed holopulp system is the need to use a ClO_2 process which does not involve sulfuric acid (as practically all conventional processes do). ClO_2 generating processes which employ HCl do exist and are sometimes called Kesting processes. Several of these are in operation overseas. The main reaction in the hydrochloric acid processes is:

$$NaClO_3 + 2HCl = ClO_2 + \frac{1}{2} Cl_2 + NaCl + H_2O$$

and it is important to minimize the side reaction:

$$NaClO_3 + 6HCl = 3Cl_2 + NaCl + 3H_2O.$$

In order to minimize the second reaction (which is wasteful of expensive chlorate) care is taken to avoid contact of excess HCl with the chlorate. Since the reactions only go under strongly acidic conditions, this normally means that the reaction of chlorate is not taken to completion. To avoid the loss of valuable chlorate, the generator can be coupled with an on-site chlorate plant to refortify the partially depleted generator effluent. The result is an essentially closed ClO_2 plant which takes in hydrochloric acid and electrical energy and yields ClO_2 (and Cl_2 if desired). This is very attractive for the holopulp system.

One commercially available system employing these concepts is the Chemetics Integrated Chlorine Dioxide Process. Chemetics has a strong position in sodium chlorate cell design, with over eleven chlorate plants sold. The integrated process, which uses the ClO_2 generator effluent in the chlorate cells to form the closed system, has been studied extensively on a laboratory and pilot

plant scale. It is not known if any of these integrated processes have been sold or put into operation. However, such a process will appear more and more attractive to bleached kraft mills as the need to limit sulfur inputs increases, and it would appear to be only a matter of time before such systems are installed. Thus, ClO_2 generation technology should be available to the holopulping process when it is required.

Another development in ClO_2 generation which may have a bearing on the holopulp system is with the Erco-R3 process. This was originally a sulfuric acid-based process which gave crystallized Na_2SO_4 as a generator effluent. They have experimented with using HCl to replace a part of the sulfuric acid in order to make the ClO_2 generator more flexible with regard to pulping make-up requirements. They have been rumored to have been able to replace all of the sulfuric acid with HCl, although no information has been published on it. If this is true, that system could also be applicable to holopulp.

HCl Burning

The combustion of chlorine in hydrogen to form HCl and scrubbing it to make hydrochloric acid is a well-established technology. It would be available to the holopulping process when needed.

CAUSTICIZING OPERATIONS

When the level of Na_2CO_3 relative to NaCl in the recovered ash is sufficiently high it would be more economical to produce some NaOH directly from the Na_2CO_3 by causticizing with lime rather than relying solely on electrolytic means. The exact amount of Na_2CO_3 which would have to be present to justify such an approach would be determined by economic considerations and is not critical to this discussion. It is anticipated that all of the recovered chemical

would be subjected to the causticizing reactions (this would convert most of the Na_2CO_3 to NaOH and leave the NaCl untouched). This resulting white liquor would then be evaporated to drop out the NaCl for subsequent electrolysis. This latter operation is basically similar to the salt purge in the Reeve-Rapson effluent-free kraft mill concept (6).

There are three steps necessary to the success of this operation:

1. The presence of large amounts of NaCl must not interfere with the progress of the causticizing reactions.
2. The presence of large amounts of NaCl must not interfere with lime reburning.
3. It must be possible to separate the NaCl from the white liquor.

The first point was examined earlier in this project and the results presented in Report Fifteen (3). It was found that the presence of NaCl, in proportions varying from 0 to 80% of the initial Na_2CO_3-NaCl mixture, had no appreciable effect on the conversion of Na_2CO_3 to NaOH by causticizing with lime.

The second point has not been studied directly. However, the fact that some kraft mills operate with large amounts of NaCl recirculating around their systems seems to indicate that any problems in this area can be overcome.

The third step may seem to be the most critical, but there are sound reasons for believing it can be carried out. Caustic evaporation to drop out large amounts of NaCl is a well-established aspect of diaphragm cell chlor-alkali technology. The white liquor evaporation step would be only slightly more complicated than that, because of the presence of a small amount of Na_2CO_3 due

to incomplete conversion in the causticizing step. The holopulp salt purge would be simpler than the proposed purge system in the Reeve-Rapson concept because of the absence of Na_2S.

Solubility data relevant to the salt purge problem were presented by Reeve and Rapson (6). These data clearly show that Na_2CO_3 tends to be less soluble than the NaCl, so that it will come out with the NaCl. For example, at a caustic concentration of 40%, the concentration of soluble NaCl is about 4% and that of Na_2CO_3 about 1%. Two alternatives are available for obtaining pure NaCl for electrolysis. The Na_2CO_3 in the recovered salt from the caustic evaporator could be treated with HCl. A second method, and that proposed by Reeve and Rapson, is to partially leach the recovered salt with fresh water to leave NaCl behind and recycle the carbonate-containing solution back to the green liquor. Calculations showing an example of these operations are given in Appendix VI.

There is little doubt that the technology for removal of sodium chloride from white liquor by evaporation and crystallization will be available when needed for holopulp recovery. Erco Envirotech Ltd., a joint venture company between Erco and Envirotech Corporation is currently involved in the commercial development of the Reeve process for NaCl purging from kraft white liquor.

OVERALL STATUS OF RECOVERY

On the basis of the work which has been completed it can be concluded that workable chemical recovery systems for holopulp will be available when required. No new technical breakthroughs are required. For the most part, existing technology will be used. Chlorine dioxide, chlorine, hydrochloric acid, and caustic production will be drawn from commercially proven systems. Evaporation and incineration of the spent liquors will involve the direct use of (or reasonably short extrapolations from) equipment and processes normally used for these purposes. There appear to be no technical roadblocks to successful chemical recovery.

It appears that there are basically two recovery concepts which are workable. The choice between the two is determined by the pulping stoichiometry used and the resultant proportions of sodium and chlorine in the spent liquor. The major elements of these systems are as follows:

1. System with high chlorine levels (Na/Cl about 1).
    a. Evaporation to about 40% solids.
    b. Fluidized bed incineration to produce NaCl, (HCl scrubbing from flue gas may be needed).
    c. Electrolysis of NaCl to form Cl_2, H_2, and NaOH.
    d. Burning H_2 and Cl_2 to form HCl.
    e. ClO_2 production from integrated process.
2. System with high sodium levels (Na/Cl about 3 to 4).
    a. Evaporation to 60-65% solids.
    b. Combustion in soda-type recovery furnace to recover a $NaCl$-Na_2CO_3 mixture.

c. Causticizing the mixture followed by white liquor evaporation to drop out NaCl.

d. Electrolysis of NaCl to form Cl_2, H_2, and NaOH.

e. Burning H_2 and Cl_2 to form HCl.

f. ClO_2 production from integrated process.

Flow sheets illustrating each of these processes are shown in Fig. 5 and 6, respectively.

In addition to these full-blown recovery systems, it would be possible to operate a small holopulp plant in cross-recovery with a kraft mill, by using the Reeve process of white liquor evaporation and crystallization to remove NaCl from the kraft cycle. It would also be possible to operate a holopulp system in open-loop fashion by disposing of the chemicals after incineration. These approaches would open the door to the use of sulfur in the pulping process. However, disposal problems could be severe, and production rates would probably be limited. These approaches could be quite attractive in a fairly large pilot plant or semicommercial venture.

Studies on recovery for holopulp appear to have reached a point of diminishing returns unless there is a significant increase in scale. Questions which remain regarding incineration, evaporation, and salt purity cannot be adequately answered without pilot tests using relatively large quantities of actual pulping spent liquors. Other questions about the process, such as the ability to recover the liquor solids at reasonable concentrations, and the possibility of tall oil and turpentine recovery in softwood pulping, practically demand a pilot-scale pulping operation for their resolution. The work carried out at laboratory scales has shown that recovery systems should be quite feasible. The next major steps in this area would have to be at the pilot plant level.

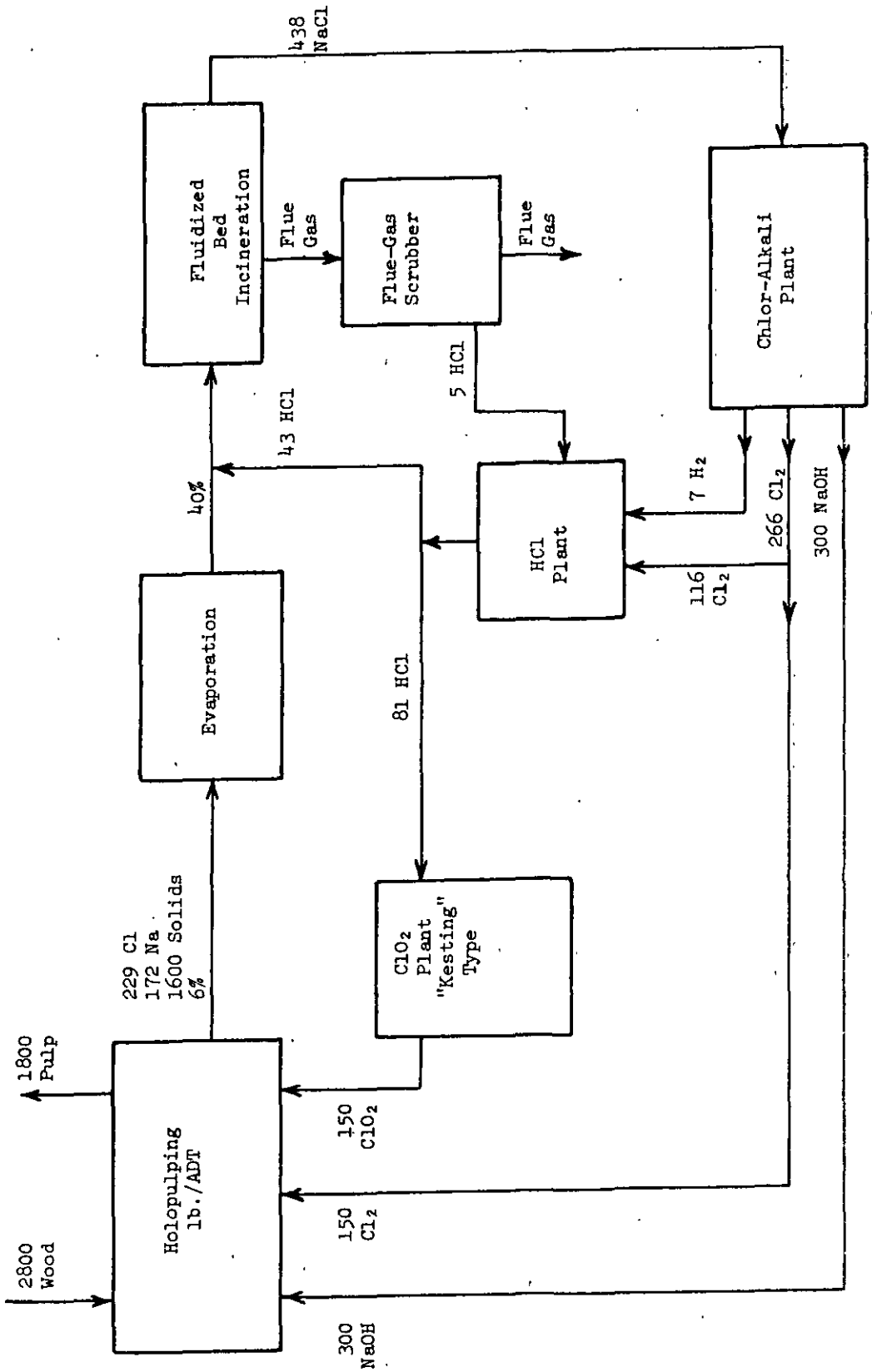

Figure 5. Flow Sheet for Chlorine Rich Recovery System

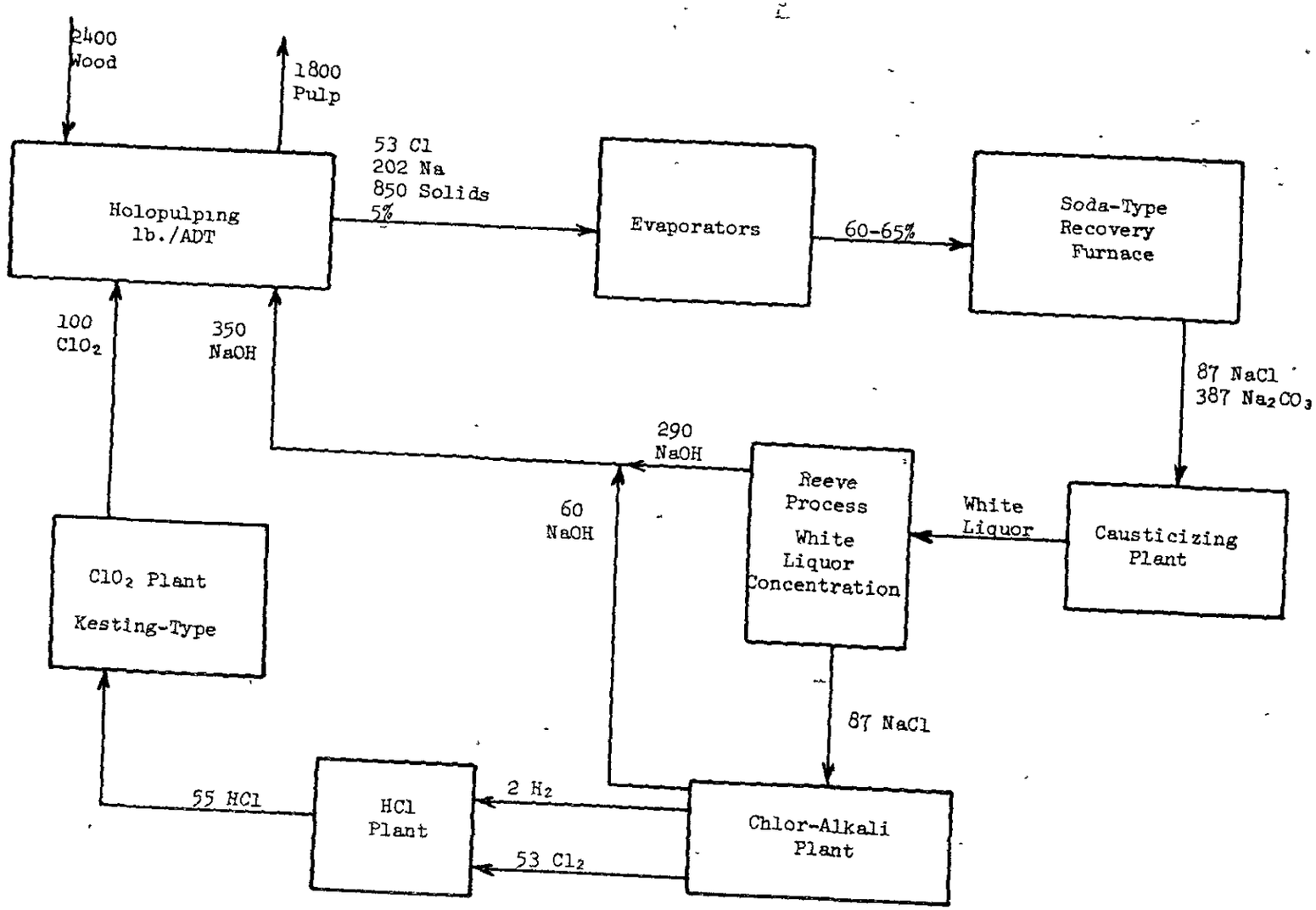

Figure 6. Flow Sheet for Sodium Rich Recovery System

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APPENDIX I

DESCRIPTION OF FLUIDIZED BED TEST LOOP

The fluidized bed test system described in Report Fifteen (3) was totally rebuilt for the tests carried out in this program. The new system provides compressed, indirectly heated air to an electrically heated test bed. Thus, the problems associated with high heat losses and the flow oscillations in the old system were eliminated.

A schematic diagram of the new system is shown in Fig. 7. The main components of the system are an air compressor, an indirect air heater, the test bed itself, liquor supply system, a cyclone for solids removal, and a wet scrubber.

The fluidized bed is contained within a ceramic tube, 4-1/8" I.D. x)" long. The ceramic tube, in turn, is inserted within a tubular electric rnace to control heat losses. Hot air is distributed across the bottom of e bed through a restriction plate similar to that described in Report Fifteen). A pipe is inserted through the bottom of the plate to permit removal of lids from the bed. It was capped off from the outside in all of the tests ich have been completed. Thermocouples are used to measure the temperature the incoming air, at two locations within the bed, and in the freeboard zone. ssures are measured in the entrance plenum, at the bottom of the bed, and in freeboard area.

Liquor is introduced to the bed from a nozzle located directly above 30-inch test zone. Liquor drips from the feed gun and falls to the bed e it ignites. A variable speed "fingering" pump, squeezing tygon tubing, was upply the liquor at controlled rates. Flow was measured by pumping from a

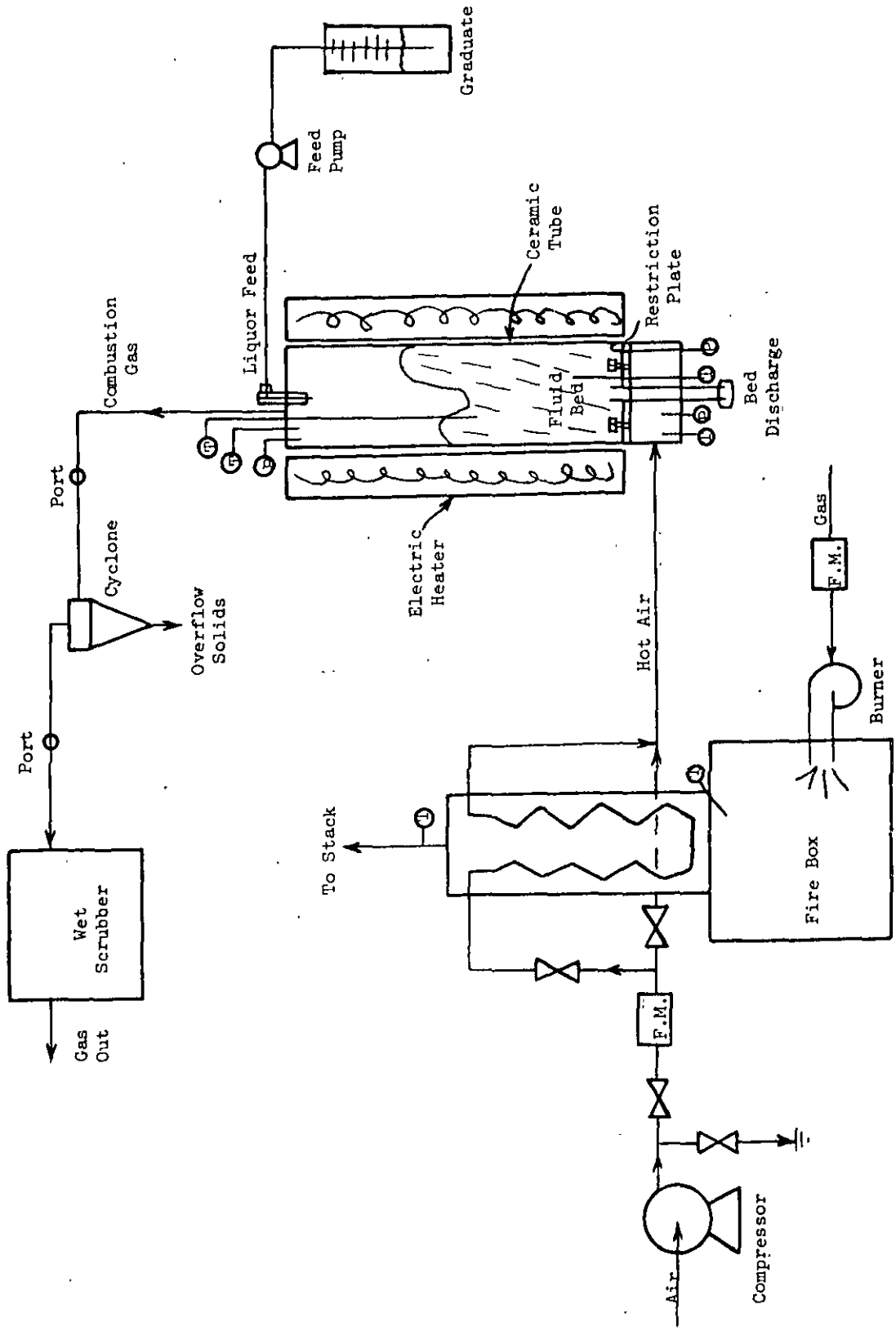

Figure 7. Diagram of Fluidized Bed Test Loop

graduated cylinder and using a stopwatch. The graduate was periodically refilled by hand from a holding tank.

Operation of this system is quite straightforward. A charge of salt (or other bed material) is added and air flow established. The air heater and electric heater are then turned on and the system brought up to operating temperature. When the desired temperature level is reached, the feed is started and rates adjusted. Temperatures will then climb until steady-state is reached. Operation can continue indefinitely as long as adequate fluidization can be maintained. Fresh bed material can be added to the system through the feed port to replace carryover losses. Although provisions were made for removal of bed material underflow during operation, this port on the system has not been used.

APPENDIX II

PREPARATION OF LIQUOR FOR FLUID BED TESTS

It was estimated that the fluidized bed test program could require about 100 lb. of liquor solids. This would require the treatment of about 200 lb. of wood and would produce about 130 lb. of pulp. It was decided that it was not feasible to produce the amount of liquor needed by treating 1000-g. batches of fiberized wood in plastic bags, and that a significant scale-up would have to be made.

The objective of this operation was to obtain spent liquor, and relatively little attention was given to the quality of pulp produced. The liquor was produced in a three-stage operation:

1. Fiberization in the Institute double-disk refiner.
2. Oxidation with 9% ClO_2 to exhaustion.
3. Extraction with 10.5% NaOH.

The oxidation was carried out in batch fashion in a large plastic wading pool. Approximately 200 lb. of fiberized maple chips were placed in the pool. Chlorine dioxide was generated continuously in a small "Solvay" (methanol process) pilot reactor which was specially constructed for this purpose. This generator had a capacity of about 1.2 lb. of ClO_2 per hour, and the ClO_2 solution was pumped to the pool as fast as it was generated. The material in the pool was occasionally turned over with shovels to try to get even treatment. A total of about 16-1/2 lb. of ClO_2 was put on the wood. There was no temperature control in this step. The pool was located outside, covered with a plastic cover, while the reaction went to completion.

After the ClO_2 was exhausted, the pulp was dewatered and the liquor stored in a second large plastic pool. The pulp was then treated with caustic in a hydrapulper in two batches. The first batch at about 60°C. and the second at about 75°C. The hydrapulper was turned on only to achieve an initial mixing of the pulp and the caustic solution. Following the extraction, the pulp was dewatered and washed, and the liquor added to the oxidation liquor in the large pool. About 800 to 900 gallons of weak liquor at a solids content of 1% was obtained.

The weak liquor was concentrated to 52% solids in a Struthers-Wells crystallizer-evaporator which was modified to act as a normal, forced circulation evaporator. No difficulties were encountered during this concentration. Foaming was not a problem. The only odor noticeable was a slight one, reminiscent of the smell of burnt wood. About 125 lb. of concentrated liquor were obtained. After saving a sample of this concentrated liquor, 117 lb. of 52% liquor (61 lb. of liquor solids) was available for further treatment.

In order to obtain the slight excess of chlorine in the liquor needed for the fluid bed tests, it was necessary to add hydrochloric acid to the liquor. This was carried out in two steps. Initially, 20 lb. of 37% HCl was added to the liquor. A sample was then taken, dried and ashed. The ash tested out at 4.2% Na_2CO_3 and 92.2% NaCl. Based on this analysis, 3-3/4 lb. more 37% HCl was added. This was sufficient to provide a 2% excess of chlorine in the liquor.

During acidification of the original liquor, some acetic acid was driven off. This did give the acidified liquor a fairly pungent smell in close proximity. It also caused solids determinations based on oven drying to tend to be low. The viscosity of the liquor dropped significantly after acidification, and the acidified liquor at 46-48% solids could be pumped easily at room temperature.

The liquor was analyzed on a wet basis to contain 14.9% carbon, 7.4% hydrogen, and 10.3% chlorine. Using the measured solids content of 46% and the fact that the sodium was 98% of the chlorine mole for mole, gives the following elemental composition for the dry solids:

C = 32.4%

H = 3.0%

Cl = 22.3%

Na = 14.2%

O = 28.0%.

These values of the elemental composition, and a specific gravity of 1.266 were used in material balance calculations.

APPENDIX III

FLUIDIZED BED TEST RESULTS

Two runs were carried out with the holopulp spent liquor described in Appendix II. These two runs were essentially continuous. The first run terminated when the bed defluidized. This first bed was then dumped, and fresh salt added to form a new bed. Feed and air rates were then adjusted to a new set of conditions and operation continued. This constituted the second run. This run also terminated in a defluidization. When an attempt was made to dump the second bed while the system was still hot, the ceramic tube containing the bed was cracked. Thus, a third run at higher temperatures has not yet been made.

The first run was carried out at bed temperatures of about 1175°F. The bed was heated externally for about two hours to reach about 1000°F. before liquor firing was initiated. It then required another 3 hours to reach a stable operating condition at the 1175°F. level. About 5 hours of good stable operation were then achieved. Conditions during this interval were as follows:

Liquor feed rate	23 to 28 cc./min.
Fluidizing velocity	2.4 ft./sec.
Bed temperature	1175 to 1180°F.
Freeboard temperature	1060 to 1090°F.
Inlet air temperature	610°F.
Flue gas composition	5.7 to 6.8% CO_2
Average carbon burnup	82%.

Toward the end of this period the bed began to get sluggish and finally defluidized. At this point feed was cut off and air flow increased. The bed was refluidized by poking with an iron rod through the feed gun port. Some

fresh salt was added also. Feed was off for about an hour. When operation was reestablished, it was with a fluidizing velocity of 3.1 to 3.2 ft./sec. and a feed rate of 19 to 20 cc./min. This led to bed temperatures of about 1150°F. Operation was maintained at this condition for about 3-1/2 hours before the bed defluidized again. During this period the average carbon burnup dropped to 67%. After the second defluidization, behavior was very marginal and the run was terminated by dumping the bed.

Examination of the dumped bed material showed it to be significantly greater in particle size than the starting bed material. These were agglomerates of the original salt particles. Test for carbonate on this material were negative.

The dumped bed and more particularly, the overflow solids, were dirty because of the presence of some carbonaceous matter. Samples were taken and tested for filterable solids (which were assumed to be carbon). During the steady period, "insoluble" material range from 1.2 to 1.7% (a blank, using pure salt, gave 1.2%). After the defluidization crisis, values ran from 2.5 to 3.5%.

A material balance on salt over the entire run is as follows:

Inputs		Outputs	
Starting bed	3570 g.	Final bed	2210 g.
Salt added to bed	2170 g.	Overflow	6075 g.
Salt in liquor fired	3570 g.	Scrubbed in tower	1200 g.
	10,240 g.		9485 g.

The new bed was started with 2600 g. salt, and was heated up for 50 minutes before firing liquor. Steady conditions were reached about 1 hour after

starting liquor feed. Four hours of very steady running were then obtained. During this interval the following conditions existed:

Liquor feed rate	25 to 28.5 cc./min.
Fluidized velocity	3.1 ft./sec.
Bed temperatures	1210 to 1220°F.
Freeboard temperature	1090 to 1120°F.
Inlet air temperature	675°F.
Flue gas composition	5.8 to 6.4% CO_2
Average carbon burnup	95%.

After this time period, the fluidizing began to get sluggish. The air rate was gradually increased to 3.9 ft./sec. and bed temperatures fell to about 1200°F. Operation was continued for another 3-1/2 hours before final defluidization.

The characteristics of the particles removed from the bed after the second run were very similar to those from the first bed. Analysis of "insoluble" material in the overflow gave 2.9% at the end of the steady period and 3.5% during the gradual defluidization period. This latter sample also tested out at 94.5% NaCl.

Material balance for this second run is as follows:

Inputs		Outputs	
Starting bed	2600 g.	Final bed	2700 g.
Salt added	300 g.	Overflow	3570 g.
Salt in liquor fired	3420 g.	Scrubbed in tower	630 g.
	6320 g.		6900 g.

APPENDIX IV

SUMMARY OF TESTS AT BABCOCK AND WILCOX

Two liquors were sent to Babcock and Wilcox and designated Liquor A and B. These were prepared as follows from fiberized maple chips:

Liquor A:	Oxidation	–	9% ClO_2
	Extraction	–	9% NaOH
	Bleach	–	3% Hypochlorite
Liquor B:	Pretreatment	–	6% NaOH
	Oxidation	–	4% ClO_2
	Extraction	–	6% NaOH
	Bleach	–	3% Hypochlorite.

In both cases, the liquors from the individual steps were collected and combined. These dilute liquors were concentrated to about 10% solids before being sent to B & W. Due to delays in contract negotiations, the liquors were stored at B & W for about four months before the tests were run.

Basic analyses of these liquors are given in Tables I and II. Emission spectrographic analysis of the ash showed major amounts of sodium and some calcium, magnesium, and iron. No other metals were present in significant quantities.

Viscosity and specific gravity data for these liquors are given in Table III. Viscosities were determined with a Brookfield viscometer.

Thermogravimetric analyses were run on the liquors. The shapes of the weight vs. temperature curves were very similar to kraft. A relatively

TABLE I

ANALYSIS AND HEATING VALUE OF LIQUOR A

Basis (ovendry)	As-Received		Concentrated	
	Wet	Dry	Wet	Dry
Mositure, %	88.8	0.0	53.0	0.0
Solids	11.2	100.0	47.0	100.0
Total sodium, Na_2O, %	--	--	8.8	18.7
Total chlorine, Cl, %	1.90	17.0	7.5	16.0
Chloride, Cl, %[a]	1.17	10.4	5.3	11.3
Gross heating value, Btu/lb.	--	--	2690	5720

Ultimate Analysis — Elemental

Basis (ovendry)	Wet	Dry
Moisture, %	53.0	0.0
Carbon	16.8	35.7
Hydrogen	1.4	3.0
Chlorine, Cl	7.5	16.0
Sodium, Na	6.5	13.8
Inerts	0.6	1.3
Oxygen, by diff.	14.2	30.2
Total	100.0	100.0

[a] Water soluble.

TABLE II

ANALYSIS AND HEATING VALUE OF LIQUOR B

Basis (ovendry)	As-Received		Concentrated	
	Wet	Dry	Wet	Dry
Moisture, %	91.25	0.0	53.6	0.0
Solids	8.75	100.0	46.4	100.0
Total sodium, Na_2O, %	--	--	12.2	26.3
Total chlorine, Cl, %	1.02	11.7	5.2	11.2
Chloride, Cl, %[a]	0.82	9.4	4.8	10.3
Gross heating value, Btu/lb.	--	--	2360	5090

Ultimate Analysis — Elemental

Basis (ovendry)	Wet	Dry
Moisture, %	53.6	0.0
Carbon	15.0	32.3
Hydrogen	1.4	3.0
Chlorine, Cl	5.2	11.2
Sodium, Na	9.0	19.4
Inerts	0.3	0.6
Oxygen, by diff.	15.5	33.5
Total	100.0	100.0

[a] Water soluble.

TABLE III

VISCOSITIES AND SPECIFIC GRAVITIES

Liquor	Solids, %	Temperature, °F.	Specific Gravity	Spindle Speed, r.p.m.	Viscosity, cp.
A	29.0	210	(Foam)	30	72.0
		193	1.13	30	87.0
		180	1.14	30	98.0
A	48.6	200	(Foam)	12	1700.0
				6	2500.0
		184	(Foam)	60	650.0
				30	880.0
				12	1250.0
		160	1.27	60	805.0
				30	960.0
				12	1315.0
A	59.6	185	(Foam)	60	3950.0
				30	5100.0
				12	7000.0
		170	1.29	60	5400.0
				30	6800.0
				12	10000.0
		160	1.29	60	6600.0
				30	8600.0
				12	12500.0
B	29.8	208	1.14	60	9.0
		194	1.15	30	12.0
		180	1.16	30	15.0
B	47.2	201	1.27	30	135.0
				12	194.0
				6	280.0
		190	1.27	60	116.0
				30	143.0
				12	209.0
		176	1.28	60	136.0
				30	165.0
				12	225.0
B	63.8	205	1.38	60	1300.0
				30	1840.0
				12	3000.0
		190	--	60	1600.0
				30	2200.0
				12	3750.0
		175	1.39	60	2030.0
				30	2900.0
				12	4500.0

rapid weight loss at about 700°C. is characteristic of both black liquor and holopulp liquor. This occurs about 50°C. lower for holopulp liquor and is less precipitous.

A quantitative interpretation of the TGA curves is presented in Table IV. The moisture content of the liquor is considered the weight loss up to the first breakpoint in the curve. The volatile matter (VM) is that lost up to 600°C. less the moisture. The fixed carbon (FC) is that lost in the 600-800°C. range. The remainder is considered ash. The VM, FC, and ash content of Liquor B is very similar to kraft. Liquor A is different, having higher VM and FC and lower ash. The volatiles ratio (VR) equals VM/FC and is considered an ease-of-combustion index for waste fuels. The VR ratios for holopulp liquors are at the high end of the spectrum for black liquors, which normally range from 80 to 110.

The results of the computer simulations are shown in Table V.

TABLE IV

QUANTITATIVE INTERPRETATION OF TGA CURVES

Sample Identification	As-Received Basis, wt. %				Dry Basis, wt. %			Dry, Ash Free Basis, wt. %		Volatile Ratio[b]
	H_2O	VM	FC	Ash[a]	VM	FC	Ash	VM	FC	VR
F-629, Sample "A" holopulp liquor from The Institute of Paper Chemistry (concd. to ∿50% solids)	53.0	14.9	13.3	18.8	31.7	28.3	40.0	52.9	47.2	112
	53.0	17.0	13.0	17.0	36.2	27.6	36.2	56.8	43.3	131
Av.	53.0	16.0	13.2	17.9	34.1	28.1	38.1	55.2	45.5	121
F-630, Sample "B" holopulp liquor from The Institute of Paper Chemistry (concd. to ∿50% solids)	53.6	12.1	9.8	24.5	26.1	21.2	52.9	55.3	44.9	123
	53.6	10.8	10.1	25.5	23.3	21.8	55.1	52.0	48.6	107
Av.	53.6	11.4	10.0	25.0	24.6	21.6	54.0	53.3	46.6	114

[a] By difference, not ultimate.

[b] $VR = 100 \times \frac{VM}{FC}$, This ratio is constant for a given liquor on an as-received dry, or dry ash-free basis. Thus, the ratio can be used to compare all liquors directly without making calculations to correct for moisture or ash contents.

TABLE V

COMPUTER SIMULATION OF FIRING KOLOPULP LIQUORS

Run No.	Liquor	Comments	Liquor to[a] Furnace, lb./hr.	Suppl. Fuel, No. 6 Oil, lb./hr.	Liquor Solids, %	Smelt[b] Recycle, lb./100 lb. liquor to furnace	Combust.[c] Air, lb./100 lb. liquor	Air Temp., °F.	Primary Air, % of total	Smelt Flow, lb./100 lb. liquor	NaCl in Smelt, wt. %	Flue Gas, lb./100 lb. Liquor	Flue Gas, SCF/100 lb. Liquor	H_2O in Flue Gas, vol. %	CO_2 in Flue Gas, vol. %	O_2 in Flue Gas, vol. %	HCl in Flue Gas, p.p.m. (dry)	Particulate from Furnace, lb./100 lb. liquor	Dust Load[d] at Furnace Exit, grain/SCF	NaCl in Particulate, wt. %	Heat Avail. for Steam, Btu/100 lb. liquor	Run No.
1	A	"Normal" kraft firing	92,100	—	62.0	0	276	300	50	0.00	—	358	4620	25.1	14.0	2.1	21	21.2	42.5	76.7	291,400	1
2	A	Lower air temp. and less primary air	92,100	—	62.0	0	276	70	40	0.00	—	358	4620	25.1	14.0	2.1	21	21.2	42.5	76.7	273,700	2
3	A	Less primary air	92,100	—	62.0	0	276	70	30	0.83	71.0	358	4620	25.1	14.0	2.1	21	20.4	40.5	77.2	270,600	3
4	A	Oil support for total of 9000 Btu/lb. dry	44,580	9,550	60.0	0	602	300	—	—	—	584	7404	18.7	13.2	2.2	19	22.2	20.0	74.6[e]	517,500	-
5	B	"Normal" kraft firing	103,500	—	62.0	0	247	300	50	3.37	19.1	322	4210	27.3	12.9	2.0	8	25.2	57.5	42.5	244,300	5
6	B	Lower air temp. and less primary air	103,500	—	62.0	0	247	70	40	9.22	28.8	322	4210	27.2	13.0	2.0	10	18.7	42.3	49.2	217,700	6
7	B	Less primary air	103,500	—	62.0	0	247	70	30	14.9	32.0	322	4210	27.2	13.0	2.0	11	13.6	31.0	52.4	215,800	7
8	B	Higher air temp.	103,500	—	62.0	0	247	400	50	3.00	19.2	322	4210	27.3	12.9	2.0	8	25.6	58.2	42.2	250,500	8
9	B	More primary air	103,500	—	62.0	0	247	300	60	3.00	17.9	322	4210	27.3	12.9	2.0	8	25.5	58.2	42.3	246,000	9
10	B	Higher air temp. and more primary air	103,500	—	62.0	0	247	400	60	2.54	18.0	322	4210	27.3	12.9	2.0	8	26.0	59.2	41.9	252,300	10
11	B	Low air temp. and primary air with smelt recycle	127,300	—	69.1	18.7	201	70	40	24.6	32.0	262	3428	27.2	13.1	2.1	13	14.6	26.0	55.3	171,500	11
12	B	Low air temp. and primary air with smelt recycle	122,100	—	67.8	15.2	209	70	40	22.9	27.9	273	3573	27.1	13.1	2.0	11	13.8	37.0	51.6	180,400	12
13	B	Lower primary air with smelt recycle	127,300	—	69.1	18.7	201	70	30	30.7	31.0	262	3428	27.2	13.1	2.0	11	9.3	26.0	51.7	171,500	13
14	B	Oil support for total of 9000 Btu/lb. dry	42,500	10,800	60.0	0	637	300	—	—	—	578	7531	18.7	12.6	2.2	6	29.3	25.4	39.1[e]	514,700	14

[a] Includes recycled smelt, if any. Calculated at 400 kraft Btu-tons per day heat input.

[b] Quantity and composition of smelt was estimated prior to the computer run. Composition assumed was 40% NaCl (balance Na_2CO_3) in Run 11 and 30% NaCl in Runs 12 and 13.

[c] Calculated at 115 percent theoretical air, assuming all Cl in liquor burns to NaCl and excess Na burns to Na_2CO_3.

[d] A substantial part of this dust (we believe on the order to 50 percent) will probably be collected in the boiler hoppers, and will therefore not appear at the boiler exit.

[e] Addition of oil support causes the dust to contain about ten percent Na_2SO_4.

APPENDIX V

VISCOSITY OF HOLOPULP LIQUOR

One of the significant aspects of the tests run at Babcock and Wilcox was the finding that holopulp liquors have substantially higher viscosities than are typical of kraft. Because of the importance of liquor viscosity in concentration and incineration, it was felt necessary to determine if high liquor viscosities were inherent in holopulping, and what could be done about them.

A hardwood (maple) holopulp spent liquor was prepared to be similar to Liquor A which was sent to B & W. The pulping process consisted of a single oxidation stage using 9% ClO_2 on the wood and a single extraction stage using 10.5% NaOH on the wood. The liquors were collected, combined and concentrated to about 12% solids in a laboratory natural circulation evaporator, and then concentrated to about 40% solids in a rotary vacuum evaporator. This liquor had an ash content of 29.2%, with the NaCl content 52.4% of the ash and the Na_2CO_3 content at 44.3%.

The viscosity of this liquor was determined with a Brookfield viscometer at 41.4% solids and a temperature of 170°F., and found to be 525 centipoise. This is comparable to the viscosities measured on Liquor A by Babcock and Wilcox and indicates that their high values were not caused by the long storage time before the tests were run.

In the tests run by B & W, Liquor B had lower viscosities than Liquor A. This liquor had a higher inorganic content, a greater ratio of sodium to chlorine, and a higher pH. To see if a pH change could cause a lowering of the viscosity,

caustic was added to the concentrated liquor described above. Thirty cc. of 50% caustic was added to 250 cc. of the concentrated liquor. This was followed by another 20 cc. of NaOH. The results were as follows:

Sample	Liquor	L + 30	L + 30 + 20
% solids	41.4	40.4	40.0
Temp., °F.	175-165	175-170	175-170
Viscosity, cp.	525	70-80	29
Ash, %	29.2	42.2	49.3
NaCl, % on ash	52.4	31.7	22.8
pH	5.8	12.2	12.2+

A marked drop in liquor viscosity was noticeable as soon as the caustic was stirred into the liquor. Thus, it appears that the viscosity problem can be minimized by raising the pH of the liquor. The amount of NaOH required to do this could run as high as 20% on the liquor solids.

It is also possible to get a major drop in liquor viscosity by lowering the pH. This was clearly evident during the acidification of the spent liquor for the fluidized bed tests.

APPENDIX VI

CALCULATIONS ON SALT PURGING

In order to illustrate the ability to drop NaCl by concentrating the white liquor after causticizing, the following examples are given. In both cases the general conditions include the following:

750 lb. Na_2CO_3 and 250 lb. NaCl in green liquor

85% conversion during causticizing

40% NaOH
4% NaCl
1% Na_2CO_3
} in concentrated white liquor (6).

Simply carrying this through in a single operation, would give a concentrated white liquor containing

482 lb. NaOH

48 lb. NaCl

12 lb. Na_2CO_3

and the solids crystallized out would contain

202 lb. NaCl

100 lb. Na_2CO_3.

If this solid phase is to be prepared for electrolysis by reacting with HCl, 69 lb. HCl would be required, and would give 312 lb. NaCl. Electrolysis of this would give 214 lb. NaOH generated electrolytically, compared with 482 lb. obtained by causticizing.

An alternative approach is to partially leach the crystallized NaCl-$_2CO_3$ to dissolve all the Na_2CO_3 and recycle this solution to the causticizing eration. With this system the concentrated white liquor would contain:

555 lb. NaOH

55 lb. NaCl

14 lb. Na_2CO_3

d 195 lb. of NaCl would be sent to the electrolytic cell to generate 133 lb. NaOH. The crystallized Na_2CO_3-NaCl before leaching would contain:

320 lb. NaCl

115 lb. Na_2CO_3.